Nesting, spin-fluctuations, and odd-gap superconductivity in $Na_xCoO_2 \cdot yH_2O$

M.D. Johannes, I.I. Mazin, D.J. Singh, and D.A. Papaconstantopoulos
Code 6391, Naval Research Laboratory, Washington, D.C. 20375

We have calculated the one-electron susceptibility of hydrated Na_xCoO_2 and find strong nesting nearly commensurate with a 2×2 superstructure. The nesting involves about 70% of all electrons at the Fermi level and is robust with respect to doping. This nesting creates a tendency to a charge density wave compatible with the charge order often seen at $x \approx 0.5$, which is usually ascribed to electrostatic repulsion of Na ions. In the spin channel, it gives rise to strong spin-fluctuations, which should be important for superconductivity. The superconducting state most compatible with this nesting structure is an odd-gap triplet s-wave state.

Introduction. The recent discovery of superconductivity in the layered oxide $Na_{1/3}CoO_2{\cdot}1.4H_2O$ [1] is the subject of intense experimental and theoretical research, despite its relatively low critical temperature, due to a combination of properties that suggest the possibility of a non-trivial superconducting state and/or a non-trivial pairing mechanism. These include unusual magnetic, thermodynamic, and transport properties, the apparent proximity to both structural and magnetic instabilities, and the frustrated triangular Co lattice. [2, 3, 4, 5, 6, 7]

A variety of possible pairing interactions may be relevant in this system. Structural instabilities have been reported in the non-hydrated compound [3, 8], suggesting the possibility of a related soft mode and, correspondingly, strong electron-phonon coupling. A high polarizability of water molecules may be responsible for "sandwich" type superconductivity, where the paired electrons and the pairing bosons are spatially separated[9]. Band structure calculations yield a ferromagnetic ground state[10, 11] and favor an anti-ferromagnetic state over a non-magnetic one, presaging long-range spin fluctuations that are observed at some dopings [12], Finally, and this is the central point of the current Letter, nesting properties of the calculated Fermi surface suggest the existence of strong anti-ferromagnetic spin fluctuations, which are bound to play an important role in superconductivity (as well as in the normal transport). First and foremost, they make a conventional singlet s-wave state rather unlikely.

Experimental evidence for a pairing symmetry is still inconclusive. There are reports of a lack of reduction of the Knight shift through the superconducting transition, suggesting a triplet state with vector order parameter directed out of the plane [13, 14, 15]. Density of states probes: μSR, NMR, and NQR have so far observed a non-exponential relaxation rate behavior below T_c [16, 17], inconsistent with a fully gapped state; some reported a Hebel-Slichter maximum near T_c[15, 18], suggesting a coherence peak in the DOS, while others did not find such a maximum, possibly because of impurity scattering.

Here, we calculate the one-electron susceptibility and show that it has strong structure in reciprocal space, which is not related to crystal symmetry, but is, accidentally, nearly commensurate with the lattice. This structure is robust with respect to doping and interlayer distance, and may even be responsible for the reported superstructures (as opposed to an intuitive picture relating them solely to Coulomb ordering of Na ions). The calculated spin fluctuations appear to be incompatible with either singlet or triplet BCS superconductivity, but they are fully compatible with so-called odd-gap superconductivity, with the most favorable symmetry being triplet *s*-wave. If this interaction is indeed responsible for the superconductivity, then, somewhat similarly to MgB_2, superconductivity is driven by the Fermi surface pockets which have relatively small volume (but large density of states). It is the two-dimensionality of the electronic structure that makes this possible.

Electronic structure, nesting and susceptibility. The strength of Coulomb correlations in $Na_{1/3}CoO_2{\cdot}1.4H_2O$ (subsequently called NCO) is yet unknown, but even in metals as strongly correlated as the high-T_c cuprates, LDA calculations consistently provide accurate Fermi surfaces. The one-electron band structure of the parent compound, Na_xCoO_2, is by now well understood [10, 19]. The Co *d*-bands are split by the octahedral crystal field of the surrounding oxygens into three t_{2g} bands per layer, well separated from the two e_g bands. The former further split in the hexagonal symmetry into one a_{1g} and two e'_g bands. The a_{1g} and one of the two e'_g bands cross the Fermi level, forming, respectively, a large hexagonal hole pocket around the Γ point, and six small, elliptical hole pockets. The effect of hydration on the electronic structure has been shown to be, for all practical purposes, related solely to lattice expansion [20], and we will therefore use an unhydrated, but expanded compound for our calculations. The neglected effects of Na or H_2O disorder would, if anything, further exaggerate two-dimensionality.

We have performed a tight-binding (TB) fit to our paramagnetic full-potential LAPW [21] band structure near E_f. The bond length dependence of the TB parameters was incorporated as described in Ref.[22], and used to analyze Fermi surface dependence on the interlayer distance, *c*, with the apical O height set to its relaxed value in the hydrated compound. The fits (details to be published elsewhere [23]) have an rms error

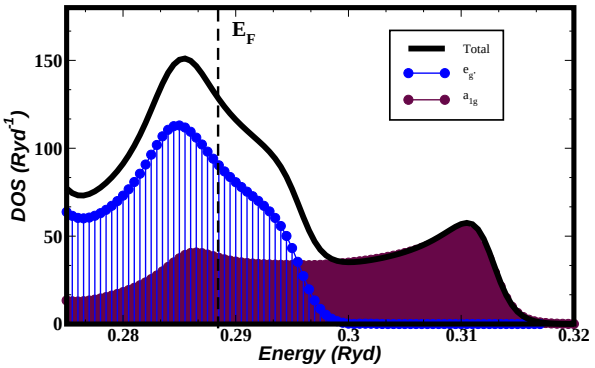

FIG. 1: (color online) The density of states of $Na_{0.3}CoO_2 \cdot yH_2O$ and of the two bands crossing the Fermi level, in the TB model [23]. The a_{1g} band, which carries 2/3 of all holes represents only about one third of N(E_F).

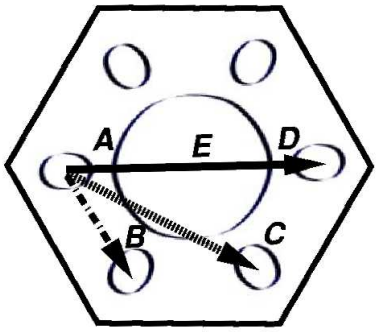

FIG. 2: The three main nesting types in $Na_{0.3}CoO_2 \cdot yH_2O$. The perfect nesting at $\mathbf{Q_1}$ is shown as a solid line and the two imperfect, $\mathbf{Q_2}$ and $\mathbf{Q_3}$, in narrow and wide dashed lines.

of only 3 mRy in the relevant energy range. This level of accuracy and a dense mesh of k-points (over 30,000 throughout the BZ) were necessary for good resolution of the very small FS hole pockets. We use the TB Hamiltonian to calculate the one-electron susceptibility $\chi_0(\mathbf{q},\omega) = \chi_0'(\mathbf{q},\omega) + i\chi_0''(\mathbf{q},\omega)$, defined as

$$\chi_0(\mathbf{q},\omega) = \sum_{\mathbf{k}} [f(\epsilon_{\mathbf{k+q}}) - f(\epsilon_{\mathbf{k}})]/(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k+q}} - \omega - i\delta),$$

where $\epsilon_{\mathbf{k}}$ is the one-electron energy, f is the Fermi function, and the matrix elements are neglected [24]. Fig. 3 exhibits the nesting structure in $\chi_0''(\mathbf{q},\omega)/\omega$ at $\omega \to 0$, important for superconductivity, and also in $\chi_0'(\mathbf{q},0)$.

With an increased c, as expected, the bands are completely two dimensional within the accuracy of our calculations. The $e_{g'}$ holes get heavier, and comprise $\sim$ 70% of the DOS at the Fermi energy (Fig. 1), though the total volume of these pockets is half the volume of the central a_{1g} pocket. The latter, which had formed a hexagonal prism with moderately flat faces in the parent compound, becomes nearly circular and, hence, its contribution to the susceptibility is practically featureless. However, the six elliptical pockets exhibit very good nesting and because of two dimensionality, their small size can only enhance the susceptibility at the nesting vector, leaving the deviation from circular cylindrical shape as the only factor determining nesting strength. Indeed, if they were exactly circular, all three nesting vectors $\mathbf{Q_1}$, $\mathbf{Q_2}$, and $\mathbf{Q_3}$, shown in Fig. 2 by solid, narrow dashed and wide dashed lines, respectively, would nest perfectly. No symmetry requirement forces these pockets to be circular, nor is there a restriction imposed on their distance from the Γ point. However, due to their small size they are nearly perfectly elliptical so that, for example, pockets A and D in Fig. 2 nest nearly exactly, and, accidentally, the distance between them is just slightly less than half of the reciprocal lattice vector $\mathbf{G}$. As a result, a strong double-humped peak appears in the calculated χ_0'' (Fig. 3) at all half-integer reciprocal lattice vectors (the distance between the humps measures the deviation of the nesting vector from $\mathbf{G}/2$).

Since $\mathbf{Q_1} \approx \mathbf{G}/2$, $\mathbf{Q_2}$ and $\mathbf{Q_3}$ are close to $\mathbf{G}/4$, as seen in Fig. 3. The corresponding peaks are suppressed by the ellipticity of the $e_{g'}$ pockets, which creates misorientation between the pockets A and B or A and C. As long as the pockets are perfect ellipses, the peaks at $\mathbf{Q_2}$ and $\mathbf{Q_3}$ have the same amplitude. In the real part of χ the peak at $\mathbf{Q_1}$ is broadened but still prominent, but the peaks at $\mathbf{Q_2}$, $\mathbf{Q_3}$ are smeared out.

Ramifications for structure and superconductivity. We have now established that there is prominent nesting-related structure in both real and imaginary parts of the electronic susceptibility at all half-integer reciprocal lattice coordinates, and weaker, but noticeable structure at all quarter-integer coordinates in the imaginary part. Because of two-dimensionality [25], in the charge channel this structure can lead to a Peierls-type charge density wave instability, *i.e.*, a structural transition. Indeed, various superstructures have been reported, especially at $x = 1/2$, and are often ascribed to charge ordering of Na ions. Our results suggest that the CoO_2 planes themselves have a tendency toward superstructure formation, even without Na ordering. The observed superstructures, presumably, are affected by both factors. Finally, there are indications [3, 8] that an antiferromagnetic ordering may set in parallel to a structural instability, which in our picture would correspond to the condensation of a spin density wave at a nesting vector.

At the compositions where the structure in χ' does *not* lead to an instability, one may expect soft modes associated with the corresponding wave vectors. However, from the point of view of superconductivity, even more interesting are the corresponding spin fluctuations, which take advantage not only of the structure in the real part of χ_0, but also of the (much sharper) structure of χ_0''. Let us first concentrate on the strongest peak in χ_0'', at

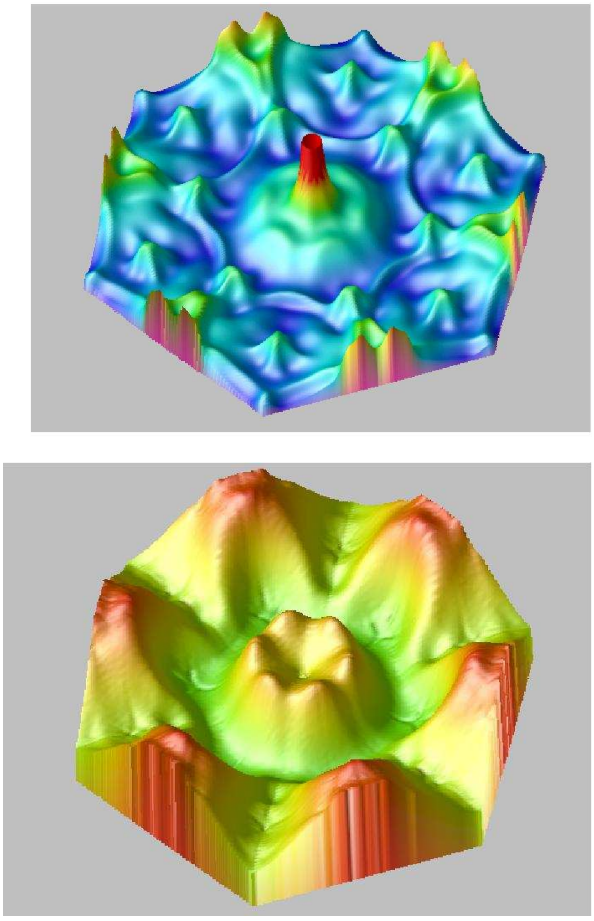

FIG. 3: (color online) *top*: $\lim_{\omega\to 0}\chi_0''(\mathbf{q},\omega)/\omega$ The double-humped peaks corresponding to $\mathbf{Q}_1$ nesting appear along the flat edges of the zone boundary. *bottom*: $\chi_0'(\mathbf{q},0)$. A temperature broadening of .001 mRy was used.

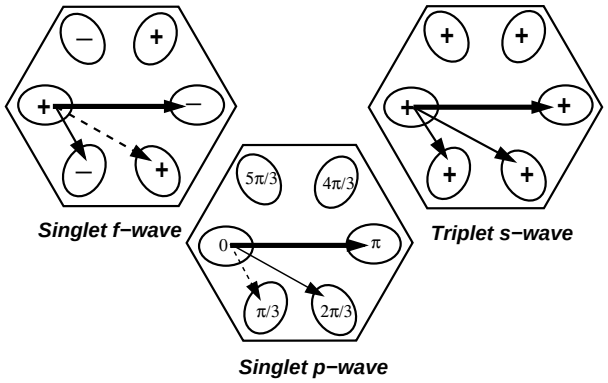

FIG. 4: The order parameter phase on the relevant sheets of the Fermi surface of various odd-gap superconducting states in NCO. Solid black lines indicate pairing interactions and dashed lines pair-breaking. In the central panel, the phase factors are $e^{i\delta}$ where δ is indicated in each pocket.

$\mathbf{q}=\mathbf{Q}_1$, and consider possible signs of the order parameter on the corresponding pockets (A and D in Fig.2). The relevant part of the linearized equation for the order parameter can be written as:

$$\Delta(\mathbf{k}_A,i\omega_n)=T\sum_{\omega_n'}\frac{V(\mathbf{Q}_1,i\omega_n-i\omega_n')}{\xi^2_{\mathbf{k}_D}+|\omega_n'|^2}\Delta(\mathbf{k}_D,i\omega_n') \quad (1)$$

Here Δ stands for the order parameter which is scalar for singlet, and vector for triplet pairing. The summation includes all Matsubara frequencies ω_n, the quasiparticle energies are given by $\xi_{\mathbf{k}}$, and $V(\mathbf{q})$ is the pairing potential (positive for attraction). For pairing induced by phonons, $V(\mathbf{q})$ is always positive, while for spin fluctuation exchange it is positive for triplet pairing and negative for singlet. Since the pockets A and D are related by spatial inversion, for inversion symmetric order parameters, s, d, *etc*, a solution to Eq. 1 exists only if $V(\mathbf{Q}_1)>0$, that is, in the triplet channel, and for antisymmetric order parameters, p *etc.*, only in the singlet channel. Note that such strict selection rules are related to the small size of the e_g' pockets. Nesting in a large Fermi surface that can support line nodes can, in principle, induce a singlet d-wave superconducting state, as discussed, for instance, in Ref. [26].

The Pauli principle forbids both singlet-p (Sp) and triplet-s (Ts) states, as well as Td, unless the order parameter is odd with respect to Matsubara time, as discussed first by Berezinski [27] for He^3, and in the context of solid state by Balatsky and collaborators [28]. In other words, spin fluctuations with $\mathbf{q}=\mathbf{Q}_1$ are pairing for the odd-gap Sp state (oSp) and for the odd-gap Ts state (oTs). The relative stability of these must be decided by other interactions. Staying within the spin-fluctuation scenario, we include now the two other nesting vectors, $\mathbf{Q}_2$ and $\mathbf{Q}_3$. Let us first consider the oS state. The order parameter is a scalar, and without loss of generality we assume it to be constant within each of the pockets, with a phase changing from pocket to pocket as in Fig 4. The lowest angular momentum solution allowed for a real order parameter corresponds to an f-wave, changing among the pockets as $\Delta_A:\Delta_B:\Delta_C:\Delta_D=1:-1:1:-1$, which implies several node lines in the induced gap on the pocket E. A complex p-wave order parameter is also allowed, so that $\Delta_A:\Delta_B:\Delta_C:\Delta_D=1:e^{i\pi/3}:e^{2i\pi/3}:-1$. In this case, the induced order parameter on the pocket E varies with angle as $e^{i\phi}$, and is nodeless, and thus energetically more favorable. Note that as long as the spin-fluctuations with vectors $\mathbf{Q}_2$ and $\mathbf{Q}_3$ couple to electrons with equal strength, they do not contribute to pairing at all in either case, canceling each other completely (because of the phase factor).

On the other hand, the oTs state can actually benefit from the two "minor" nestings. In this case, there are no symmetry-implied nodes, and the simplest so-

lution has constant gaps over both types of Fermi surfaces. The order parameters are now spinors, which can be translated in a standard way into real-space vectors. Several solutions are possible with pair spins either in or perpendicular to the hexagonal plane, for instance, $\mathbf{d} = const \cdot \hat{\mathbf{z}}$, where $\hat{\mathbf{z}}$ is the unit vector in c direction, or $\mathbf{d}= const \cdot (\hat{\mathbf{x}}+i\hat{\mathbf{y}})$. Importantly, for any of the oTs states, all spin fluctuations are pairing, including those with $\mathbf{q} = \mathbf{Q}_2$ and $\mathbf{q} = \mathbf{Q}_3$. Furthermore, an oTs state seems compatible with the limited experimental information available on the pairing symmetry. First, such a state would not exhibit exponential behavior in DOS-probing experiments (specific heat, NMR/NQR, penetration depth) [16, 17]. Second, a coherence peak in the NMR relaxation rate T_c, if it exists, should be suppressed compared to a conventional eSs state. In most experiments such a peak is not observed, but a rather weak coherence peak was seen in Ref. [15, 18]. Third, specifically the $\mathbf{d} \parallel \hat{\mathbf{z}}$ triplet s-state, similar to the chiral p-state in Sr_2RuO_4, implies no change in the in-plane susceptibility, as measured by the Knight shift. [13, 14, 15]. Finally, non-magnetic impurities are not pair-breaking for an oTs state, in agreement with observation [29].

Conclusion. We calculated the bare susceptibility of $Na_{1/3}CoO_2$ in the expanded structure, corresponding to $Na_{1/3}CoO_2 \cdot yH_2O$. We found that the main contribution to the density of states comes not from the large Fermi surface pocket at the zone center, but from small surrounding pockets. These pockets exhibit strong nesting features, accidentally commensurate with the lattice, and suggest proximity to both charge and spin density wave instabilities. The structure of the spin fluctuations is such that it favors an odd-gap triplet s-wave superconductivity, which seems compatible with existing experiments. The results reported in this Letter are calculated for x=0.3, but we have verified that the described nesting features remain up to at least x=0.5.

Acknowledgments. We acknowledge valuable discussions with A. Balatsky, D. Mandrus, S. Nagler, and B. Sales. We are particularly grateful to D. Agterberg for pointing out to us the possibility of odd-gap superconductivity in connection with the nesting in this compound.

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[24] This approximation is good as long as the character of the wave functions at $\mathbf{k}$ and $\mathbf{k+q}$ is the same. This is true for a_{1g} transitions, as well as for the $\mathbf{Q_1}$ nesting. Because of the double degeneracy of the $e_{g'}$ representation, the matrix elements will be reduced for $\mathbf{Q_2}$ and $\mathbf{Q_3}$ by a factor of up to two, and strongly suppressed for the weakly-structured $a_{1g} - e_{g'}$ component. For the qualitative discussion here, however, the constant matrix elements approximation is sufficient.
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